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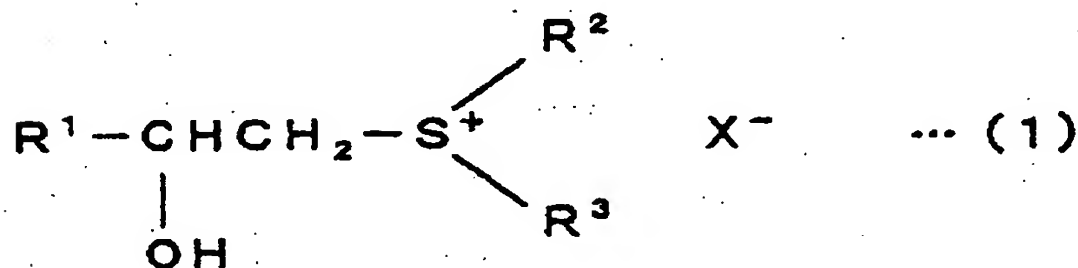
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(54) Abstract Title

Electrically conductive coating composition

(57) An electrically conductive coating composition comprises a sulfonium salt compound of the following formula (1) as an electrical conductivity-imparting agent;



wherein R¹ represents a C₈₋₂₀ alkyl group optionally containing an ether linkage or an ester linkage; R² and R³ each represents a hydroxyalkyl group containing 1 to 3 carbon atoms; X⁻ represents an anion derived from an acid compound by removal of a hydrogen atom.

The composition may also comprise an epoxy compound and the anion may be derived from e.g. a carboxylic acid or an alkyl sulfonic acid.

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TECHNICAL FIELD

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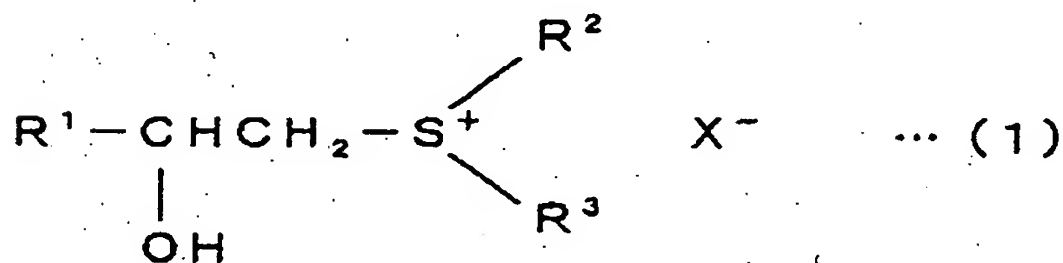
overcoating is necessarily restricted. Furthermore, the use of an electrical conductivity-imparting agent which does not interfere with the hue of the coating film, such as a quaternary ammonium salt, to a coating entailed the problem of poor water resistance of the coating film.

Therefore, the development of an electrically conductive primer which enables multi-layer electrostatic coating of plastic materials without affecting the hue of the finished coating film has been in demand.

SUMMARY OF THE INVENTION

The object of the present invention is to provide an electrically conductive coating composition which is capable of rendering plastic materials compatible with electrostatic coating, does not affect the hue of the top coat to be applied in the formation of a multi-layer coating film, and does not adversely affect the water resistance of the coating film and a method for electrostatic coating of plastic materials using said coating composition.

The electrically conductive coating composition for electrostatic coating use according to the invention comprises a sulfonium salt compound of the following formula (1) as an electrical conductivity-imparting agent.



(wherein R¹ represents a C₈₋₂₀ alkyl group optionally containing an ether linkage or an ester linkage; R² and R³ each represents a hydroxyalkyl group containing 1 to 3 carbon atoms; X⁻ represents an anion derived from an acid compound by removal of a hydrogen atom)

The sulfonium salt compound mentioned above may be obtained by reacting

a sulfide having two hydroxyalkyl groups each containing 1 to 3 carbon atoms,

5 an epoxy compound having a C₉₋₂₀ alkyl group, said alkyl group optionally containing an ether linkage or ester linkage, an acid compound and water.

10 The acid compound mentioned above may be selected from the group consisting of formic acid, acetic acid, propionic acid, sulfonic acid, methanesulfonic acid, ethanesulfonic acid, sulfuric acid, methylsulfuric acid and phosphoric acid.

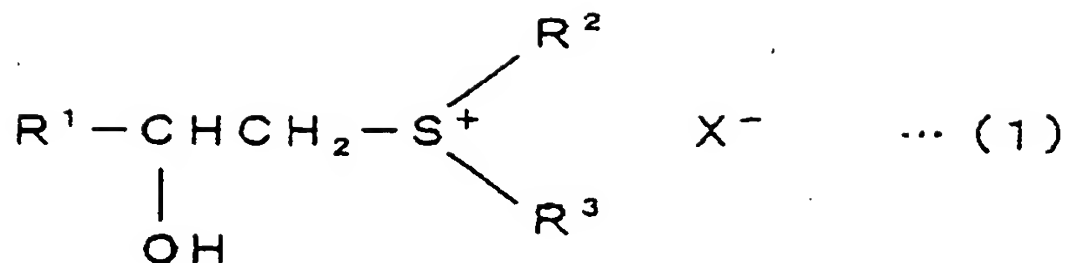
The electrically conductive coating composition for electrostatic coating use according to the invention may
15 contain the electrical conductivity-imparting agent in a proportion of 1 to 15 mass % based on the solid matter of the coating composition.

The electrically conductive coating composition for electrostatic coating use according to the invention may
20 comprise an epoxy compound, in which case the acid compound may be a carboxylic acid.

On the other hand, the method for electrostatic coating of plastic materials according to the invention comprises non-electrostatic spray-coating a plastic material with said
25 electrically conductive coating composition to form a coating film and then applying another coating by the electrostatic coating. Here, said another coating may be said electrically conductive coating composition.

30 DETAILED DESCRIPTION OF THE INVENTION

The electrically conductive coating composition of the invention contains a sulfonium salt compound of the following formula (1) as an electrical conductivity-imparting agent.



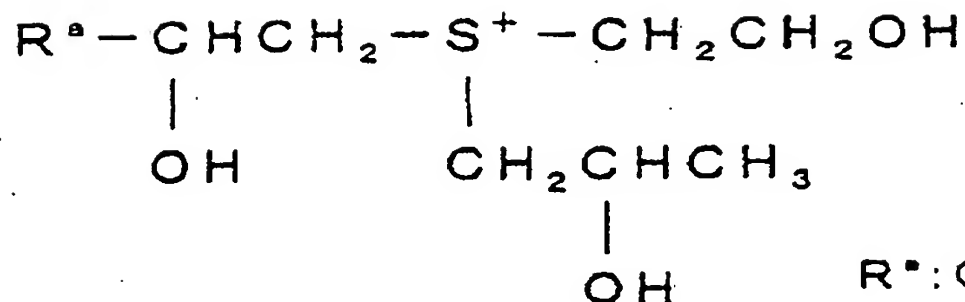
(wherein R¹ represents a C₈₋₂₀ alkyl group optionally containing an ether linkage or an ester linkage; R² and R³ each represents a hydroxyalkyl group containing 1 to 3 carbon atoms; X⁻ represents an anion derived from an acid compound by removal of a hydrogen atom)

As specific examples of the group R¹, there can be mentioned octyl, 2-ethylhexyl, decyl, dodecyl, stearyl, dodecanyl and nonyl phenyl ether, among others. It is to be understood that, in the context of this invention, alkyl aryl groups such as "nonyl phenyl ether" are subsumed in the concept of "alkyl". When the number of carbon atoms in R¹ is outside the range of 8 to 20, no sufficient compatibility with electrostatic coating can be imparted.

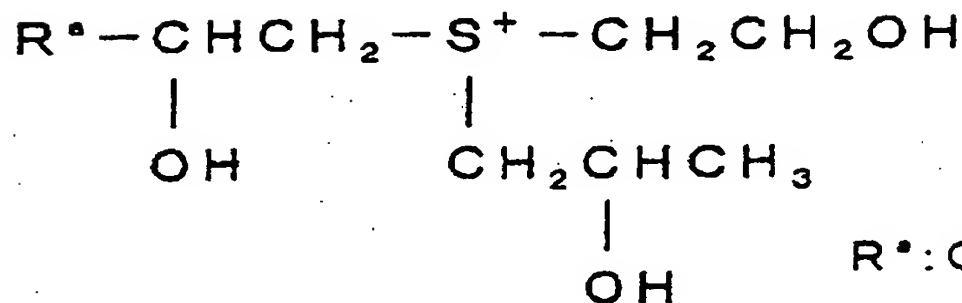
R² and R³ may be the same or different. As specific examples of said hydroxyalkyl group containing 1-3 carbon atoms, there can be mentioned hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 1,2-dihydroxyethyl, 1-hydroxypropyl, 2-hydroxypropyl, 3-hydroxypropyl, 1,2-dihydroxypropyl, 1,3-dihydroxypropyl, 2,3-dihydroxypropyl, (2-hydroxymethyl)ethyl and di(2-hydroxymethyl)methyl.

On the other hand, the acid compound mentioned above is not particularly restricted but is preferably formic acid, acetic acid, propionic acid, sulfonic acid, methanesulfonic acid, ethanesulfonic acid, sulfuric acid, methylsulfuric acid or phosphoric acid.

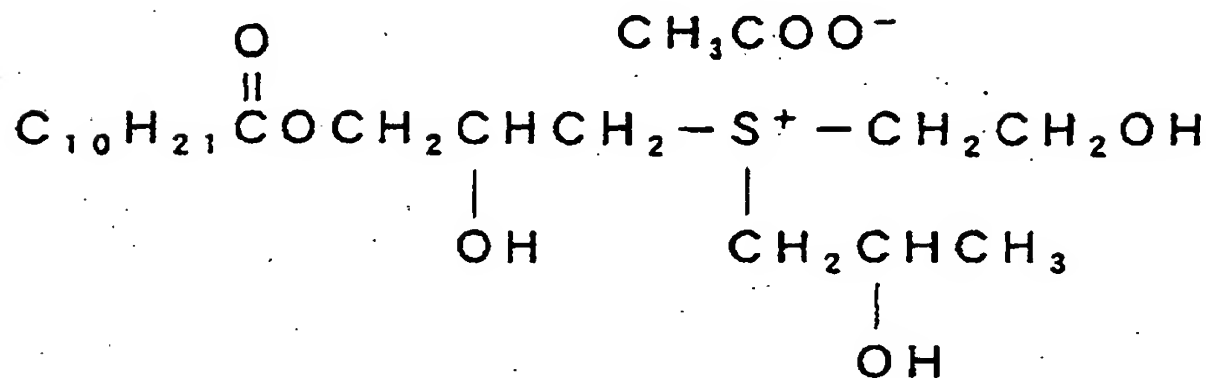
As specific examples of said sulfonium salt compound, there can be mentioned compounds having the following structures.



$\text{R}^\bullet: \text{C}_{14-16}$ alkyl group



$\text{R}^\bullet: \text{C}_{14-16}$ alkyl group



5 The sulfonium salt compound for use as said electrical conductivity-imparting agent can be obtained by reacting a sulfide having two hydroxyalkyl groups each containing 1 to 3 carbon atoms, an epoxy compound having a C_{8-20} alkyl group, said alkyl group optionally containing an ether or ester linkage, an acid compound and water.

10 This reaction can be carried out by a technique well known to those skilled in the art, for example by mixing the above-mentioned compounds in an equimolar ratio. This operation is preferably carried out under heating, at a

temperature lower than 100 °C, for accelerating the reaction. Moreover, to provide for uniform mixing, a hydrophilic organic solvent such as methoxypropanol can be added.

Since the reaction does not always proceed 100%, it is
5 good practice to terminate the reaction after a predetermined time, for example after 3 to 12 hours of reaction, and distill off the volatile unreacted material under reduced pressure. In this manner, said sulfonium salt compound can be obtained. It should be understood that the sulfonium salt compound thus
10 obtained may contain the sparingly volatile unreacted material as an impurity.

As specific examples of said sulfide having two hydroxyalkyl groups each containing 1 to 3 carbon atoms, there can be mentioned thiodimethanol, thiodiethanol,
15 thiodipropanol, 1-(2-hydroxyethylthio)-2-propanol and 1-(2-hydroxyethylthio)-2,3-propanediol, among others. As examples of said epoxy compound having a C₈₋₂₀ alkyl, alkyl ether or alkyl ester group, there can be mentioned AOE-X68 (a mixture of epoxy-terminated alkanes containing 16 to 18 carbon atoms,
20 product of Daicel Chemical Industries) and Cardura E10 (a tertiary fatty acid monoglycidyl ester, product of Shell). As examples of said acid compound, the compounds described hereinbefore can be mentioned.

The electrically conductive coating composition of the
25 present invention contains said sulfonium salt compound preferably in a concentration of 1 to 15 mass % based on the solid matter of the coating composition. If the sulfonium salt compound content is less than 1%, the required electrical conductivity will not be imparted. Conversely, as it exceeds
30 15%, the electrical conductivity is increased too much to enable satisfactory electrostatic coating.

The electrically conductive coating composition of the invention may comprise an epoxy compound. By formulating an epoxy compound, the thermal decomposition of said sulfonium
35 salt compound can be encouraged. The epoxy compound mentioned

just above is not particularly restricted. It may be a monofunctional compound or a resin having two or more epoxy groups. As examples of such epoxy compound, there can be mentioned monoepoxides such as phenyl glycidyl ether, butyl glycidyl ether, etc.; diepoxides such as ethylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, etc.; and epibis-type or novolac-type epoxy resins. Alicyclic epoxides can also be employed.

The above epoxy compound can be added as a third component but when the epoxy functional group is already available in said coating composition as it is the case with a carboxylic acid/epoxy curing system, the particular epoxy functional group can be utilized as such. The amount of said epoxy compound is preferably not less than one epoxy equivalent per equivalent of the sulfonium group of said sulfonium salt compound. If it is less than one equivalent, the objective effect may not be obtained. The more preferred range is 1 to 4 equivalents, although this does not apply when epoxy groups are already available in the coating composition.

When the electrically conductive coating composition of the present invention contains such an epoxy compound, said acid compound is preferably a carboxylic acid in view of its reactivity with the epoxy group. As preferred species of such carboxylic acid, there can be mentioned formic acid, acetic acid, propionic acid, and so on.

The application form of the electrically conductive coating composition of the invention is not restricted as far as it has sprayability. Thus, the application form may be any of the organic solvent solution type, non-aqueous dispersion type, aqueous solution type and aqueous dispersion type. The vehicle component to be formulated preferably shows good adhesion to the plastic material. Thus, for example, epoxy resin, chlorinated rubber, acrylic resin, alkyd resin, polyurethane resin, epoxy-phenol resin, silicone resin, urethane-modified acrylic resin, epoxy ester resin, etc. can

be mentioned. As mentioned hereinbefore, when the vehicle component has an epoxy group, the thermal decomposition of the sulfonium salt compound is encouraged. The composition may contain a known curing agent such as melamine and an isocyanate.

- 5 The composition containing a curing agent or a vehicle having a curable reactive group may be cured by heating or by means of actinic radiation. Furthermore, the above coating composition may optionally be supplemented with any of various organic solvents, various coating additives such as surface
10 conditioners, antisagging agents and surfactants, and pigments such as color pigments, extender pigments and metallic pigments.

While the above electrically conductive coating composition can be prepared by mixing the respective components
15 mentioned above, it can also be obtained by adding said sulfonium salt compound, optionally as well as said epoxy compound, to an existing coating. In this case, an organic solvent may be added as a diluent.

The method for electrostatic coating of plastic materials
20 according to the invention is characterized in that said electrically conductive coating composition is applied to a plastic material by non-electrostatic spray-coating to form a coating film and, then, another coating is applied by electrostatic coating.

25 The plastic materials which can be used in practicing the electrostatic coating method of the invention are not particularly restricted. For example, the method can be applied to plastic materials used as automotive bumpers, facia, fenders, hoods and trunk components, and plastic materials used
30 in household electrical appliances, precision machinery and equipment, office equipment, and so on. As compatible raw materials, there can be mentioned polyurethane resin, polypropylene resin, polyethylene resin, polystyrene resin, ABS resin, vinyl chloride resin, nylon, phenol resin,
35 polystyrene resin, polyacetal resin, polycarbonate resin, etc.,

inclusive of mixtures or modification products thereof, and even reinforced versions of said resins. The surface of the plastic material may have a primer layer formed by using a conventional primer coating.

5 The method of spray-coating with said electrically conductive coating composition is not particularly restricted but is preferably an air spray method or an airless spray method. The coating coverage is preferably 10 to 50 μm in term of dry film thickness. When the dry film thickness is less than 10
10 μm , the electrical conductivity necessary for electrostatic coating cannot be obtained. Conversely when the thickness exceeds 50 μm , the appearance is adversely affected at times. It should be understood that the coating so applied is not dried but subjected directly to the next coating operation.

15 The coating film formed in this manner is more electrically conductive than the plastic or primer surface and accepts an electrostatically applied another coating. The another coating mentioned just above is not particularly restricted and may contain the components described for said
20 electrically conductive coating composition. Furthermore, this coating is preferably a curable composition, and since the substrate is a plastic surface, it is preferred to select a composition which does not cause troubles such as deformation on heating.

25 Moreover, when an electrostatic coating is to be applied in overcoating on the coating film formed from this coating, the coating may be an electrically conductive coating composition containing said electrical conductivity-imparting agent. Of course, the coating to be first applied and the
30 coating to be subsequently applied by electrostatic coating are different in type. Thus, it is necessary that, whereas the coating to be applied first is expected to function as an undercoat, the coating to be applied electrostatically should contain a component or components contributing to the function
35 of a top coat or an intermediate coat.

The method for electrostatic coating of a plastic material according to the present invention can be carried into practice in the following two alternative modes. In one mode, the method comprises applying said electrically conductive coating composition directly to a plastic material by non-electrostatic spray-coating in the first place, then applying said another electrically conductive coating composition electrostatically to form a base coating film, applying a clear coating further to form a clear coating film, and heating said coating films in one operation to provide a composite coating film. In another mode, the method comprises using a plastic material carrying a conventional primer coating film as the substrate, applying said electrically conductive coating composition by non-electrostatic spray-coating to form a coating film, then forming a clear coating film thereon using a clear coating, and heating said coating films in one operation to provide a composite coating film.

The electrically conductive coating composition of the present invention renders plastic materials compatible with electrostatic coating, does not affect the hue of a top coat in a multi-layer coating film, and insures an improved water resistance of the coating film. Furthermore, by formulating an epoxy compound, the water resistance of the coating film after low-temperature baking can be further improved. This is presumably because the sulfonium compound used as an electrical conductivity-imparting agent in the present invention is converted to the sulfide compound by the heat of baking and loses its hydrophilicity, thus leading to an improvement in the water resistance of the coating film. In addition, in the embodiment wherein an epoxy compound is formulated, it appears that the counter anion of the sulfonium salt compound cleaves the epoxy group to form a highly basic anion whereby the activation energy for thermal decomposition is lowered to promote the decomposition.

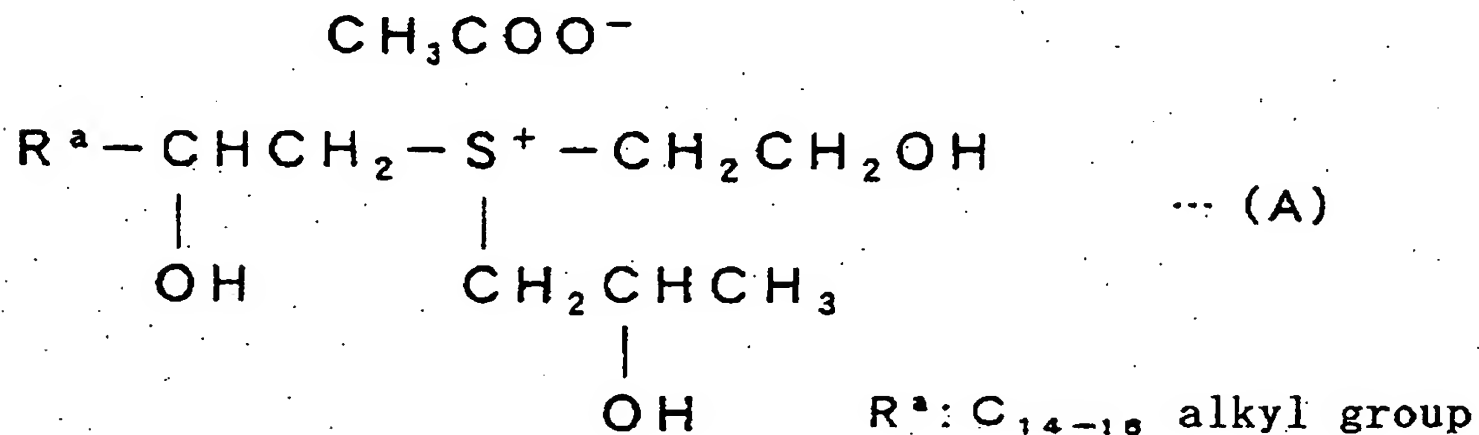
With the electrically conductive coating composition of the invention, the coating which can be used for top coating is not limited, with the result that plastic materials having various colors can be provided. Moreover, since the invention
 5 enables low-temperature baking, the electrically conductive coating composition of the invention can be applied to various substrates which are not so resistant to heat.

EXAMPLES

10 The following examples are merely intended to illustrate the present invention in further detail and should by no means be construed as defining the scope of the invention. In the examples, all parts are mass parts.

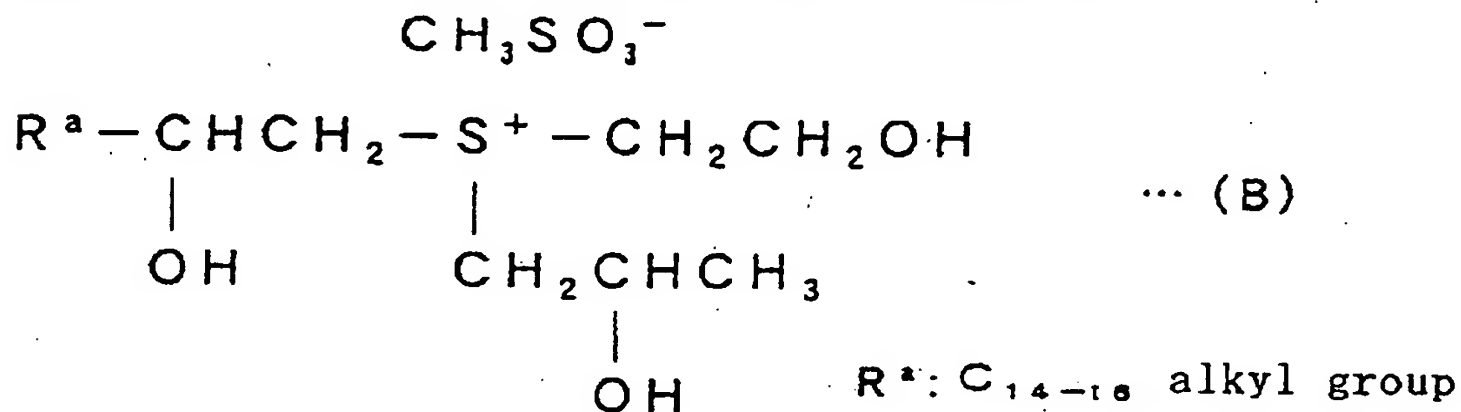
15 Synthesis of sulfonium salt compound (1)

A reactor was charged with 1 mole of AOE-X68 (an epoxy-terminated C₁₆₋₁₈ alkane mixture; product of Daicel Chemical Industries), 1 mole of SHP-100 (1-(2-hydroxyethylthio)-2-propanol; product of Sanyo Chemical
 20 Industries), 10 moles of deionized water and 1 mole of acetic acid. The charge was stirred at 90 °C for 6 hours, at the end of which time the unreacted deionized water and acetic acid were distilled off under reduced pressure to recover a solution containing a sulfonium salt compound (1) of the following
 25 formula (A). The concentration of the sulfonium salt compound in this solution was 1.0 mmol/g.



Synthesis of sulfonium salt compound (2)

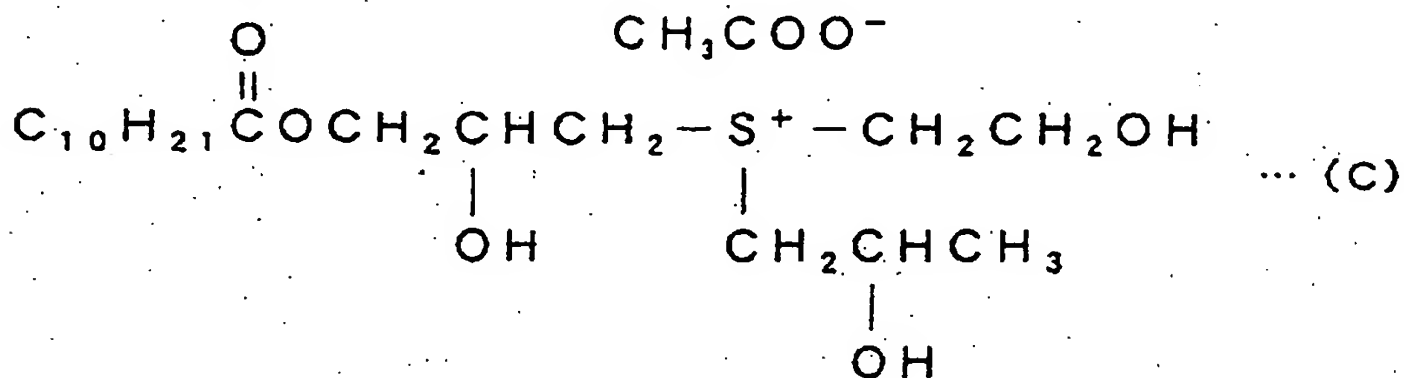
Except that methanesulfonic acid was used in lieu of acetic acid, the procedure used for preparation of said sulfonium salt compound (1) was otherwise repeated to give a solution containing a sulfonium salt compound (2) of the following formula (B). The concentration of sulfonium salt compound (2) in this solution was 2.0 mmol/g.



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Synthesis of sulfonium salt compound (3)

Except that Cardura E10 (tertiary fatty acid monoglycidyl ester; product of Shell) was used in lieu of AOE-X68, the procedure used for preparation of said sulfonium salt compound (1) was otherwise repeated to give a solution containing a sulfonium salt compound (3) of the following formula (C). The concentration of sulfonium salt compound (3) in this solution was 1.2 mmol/g.



20

Example 1

At room temperature, 6.0 parts of the solution containing sulfonium salt compound (1) prepared above, 100 parts of R-355 (an acryl-urethane primer; product of Nippon Bee Chemical, solid content: 50 mass %) and 50 parts of thinner were mixed and stirred to prepare an electrically conductive coating composition (1) as a primer. Further, in the same manner, 4.0 parts of the solution containing sulfonium salt compound (1) prepared above, 100 parts of R-333 (a base coating composition; product of Nippon Bee Chemical, solid content: 33 mass %) and 60 parts of thinner were mixed and stirred at room temperature to prepare an electrically conductive coating composition (2) as a base coating. The proportion of the electrical conductivity-imparting agent in each electrically conductive coating composition (1) and (2) is 12 mass %.

A polypropylene board was coated with the above electrically conductive coating composition (1) in a dry thickness of 30 μm by the air-spray coating technique and, then, with the electrically conductive coating composition (2) and R-298-1 (a clear coating; product of Nippon Bee Chemical) successively in dry film thicknesses of 15 μm and 30 μm , respectively by the electrostatic coating technique, followed by baking at 100 °C for 35 minutes to provide a multi-layer coating film.

Using the resulting board after cooling as the testpiece, its electrical conductivity, water resistance and hue were evaluated according to the criteria shown below. The results are presented in Fig. 1.

Examples 2 to 3; Comparative Examples 1 to 3

Except that the electrical conductivity-imparting agent used in Example 1 was changed to the species indicated in Table 1 in the preparation of electrically conductive coatings, electrically conductive coating compositions (3) to (12) were obtained. Using these coating compositions, testpieces were prepared and evaluated as in Example 1. The results are

presented in Table 1.

Table 1

	Example			Compar. Ex.		
	1	2	3	1	2	3
Primer	(1)	(3)	(5)	(7)	(9)	(11)
Base coating	(2)	(4)	(6)	(8)	(10)	(12)
Electrical conductivity-imparting agent	Sulfonium compound (1)	Sulfonium compound (2)	Sulfonium compound (3)	FKA-LP 8660	Catimine DM-20EH conc.	PRINT EX XE-2
Electrical conductivity	○	○	○	○	○	○
Water resistance	○	○	○	×	×	○
Hue	○	○	○	○	○	×

FKA-LP8660: product of FKA Chemical; OH-modified

5 tetraalkylammonium sulfate

Catimine DM-20EH conc.: product of Yoshimura Oil Chemical;
OH-modified tetraalkylammonium acetate

PRINTEX XE-2: carbon black; product of Degussa

10 Methods of evaluation

(Electrical conductivity)

A polypropylene board was coated with each electrically conductive coating and the resistivity value of the resulting coating film was measured and rated.

15 ○: Resistivity $< 10^3(\Omega)$

×: Resistivity $\geq 10^3(\Omega)$

(Water resistance)

20 Each testpiece was immersed in warm water at 40 °C for 10 days. The testpiece was then taken out and cross-cut to make 100 squares, 1 mm² each, and a peeling test using an adhesive tape was performed. The evaluation was based on the number of residual squares.

- : Residual squares: 100
- △: Residual squares: 90 to 99
- ×: Residual squares: 0 to 89

5 (Hue)

The L value of each testpiece was measured with Color Computer SM-7 manufactured by Suga Testing Instruments.

- : $L \geq 65$
- ×: $L < 65$

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As can be seen from Table 1, the coating film obtained by using the electrically conductive coating composition and the electrostatic coating method of the invention is excellent in electrical conductivity and the resulting multi-layer
15 coating film is excellent in water resistance and satisfactory in appearance.

Example 4

Except that, in preparing the electrically conductive
20 coating composition, the epoxy compound YDF-170 (product of Tohto Chemical; diglycidyl ether of bisphenol A) was added in such an amount that its epoxy equivalent would be equal to the sulfonium equivalent of the sulfonium salt compound (1), the procedure of Example 1 was otherwise repeated faithfully to
25 prepare an electrically conductive coating composition (13). The coating film obtained by using this electrically conductive coating composition (13) by electrostatic coating in the same manner as in Example 1 was baked at 80 °C, 90 °C or 100 °C for 35 minutes each to provide a multi-layer coating film. The
30 multi-layer coating film thus obtained and the multi-layer coating film obtained using the electrically conductive coating composition (1) of Example 1 under the comparable conditions were evaluated by the water resistance test described above. The results are presented in Table 2.

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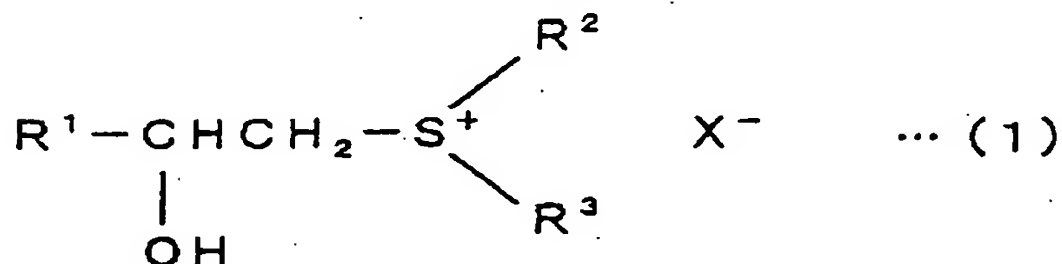
Table 2

		Example 4	Example 1
Primer		(8)	(1)
Water resistance	80 °C	○	×
	90 °C	○	△
	100 °C	○	○

It is clear from Table 2 that addition of the epoxy compound resulted in improved water resistance after low-
5 temperature baking.

CLAIMS

1. An electrically conductive coating composition comprising a sulfonium salt compound of the following formula
 5 (1) as an electrical conductivity-imparting agent;



- wherein R¹ represents a C₈₋₂₀ alkyl group optionally containing an ether linkage or an ester linkage; R² and R³ each represents a hydroxyalkyl group containing 1 to 3 carbon atoms; X⁻
 10 represents an anion derived from an acid compound by removal of a hydrogen atom.

2. The electrically conductive coating composition according to Claim 1
 15 wherein said sulfonium salt compound is obtainable by reacting
 a sulfide having two hydroxyalkyl groups each containing 1 to 3 carbon atoms;
 an epoxy compound having a C₈₋₂₀ alkyl group, said alkyl
 20 group optionally containing an ether linkage or ester linkage,
 an acid compound
 and water.

3. The electrically conductive coating composition
 25 according to Claim 1 or 2
 wherein said acid compound is selected from the group consisting of formic acid, acetic acid, propionic acid, sulfonic acid, methanesulfonic acid, ethanesulfonic acid, sulfuric acid, methylsulfuric acid and phosphoric acid.

4. The electrically conductive coating composition according to any of Claims 1 to 3

which contains said electrical conductivity-imparting agent in a proportion of 1 to 15 mass % based on the solid matter
5 of the coating composition.

5. The electrically conductive coating composition according to any of Claims 1 to 4

which comprises an epoxy compound.

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6. The electrically conductive coating composition according to Claim 5

wherein said acid compound is a carboxylic acid.

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7. A method for electrostatic coating of a plastic material

which comprises non-electrostatic spray-coating a plastic material with the electrically conductive coating composition according to any of Claims 1 to 6 to form a coating
20 film

and then applying another coating by electrostatic coating.

8. The method for electrostatic coating of a plastic
25 material according to Claim 7

wherein said another coating is the electrically conductive coating composition according to any of Claims 1 to 6.



INVESTOR IN PEOPLE

Application No: GB 0104267.0
Claims searched: 1 to 8

Examiner: Miss M M Kelman
Date of search: 25 May 2001

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): C3K KHA C3V VACD

Int Cl (Ed.7): C08J 7/04; C08K 5/36, 5/42; C09D 5/24, 5/46

Other: ONLINE: CHABS, EPODOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0576031 A1 TOYOTA JIDOSHA	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.